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A REVIEW OF CURRENT METHODS
FOR MEASURING
PARTICULATE MATTER INCLUDING CONDENSABLES
FROM STATIONARY SOURCES

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

Condensable emissions from stationary sources are of concern to the Agency in that they form a part of the overall PM_{10} ambient particulate burden. Acceptable measurement methodology is important for proper assessment of the impact on the environment of these emissions. Since no measurement method for condensable emissions has been fully developed, a review of existing methodology for the measurement of these emissions is an appropriate first step for developing a reliable method. This report describes such a review and presents recommendations for future development of a sampling method for condensable emissions.

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ABSTRACT

The PM_{10} ambient air particulate concentration standard has created a need for updating measurement methods for PM_{10} emissions (nominally $10\ \mu m$ aerodynamic diameter and smaller) from stationary sources. Condensable emissions can be a significant portion of stack emissions. Further, since these substances primarily condense to particles less than $10\ \mu m$ in diameter, they form a greater percentage of the PM_{10} fraction than of the total particulate matter emissions. Therefore, the need arises for developing a source test method which includes the condensables component of emissions. A review of possible techniques was conducted to determine current methodology and to make recommendations for research. Research is recommended on two approaches. One is a dilution method which simulates plume formation by mixing stack gases with conditioned ambient air and the other is an adaptation of utilizing the Method 5 back-half catch. This report was submitted in fulfillment of Work Assignments 3 and 15 of Contract 68-02-4442 by Southern Research Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from January 1, 1987 to September 30, 1988, and work was completed as of September 30, 1988.

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SECTION 1

INTRODUCTION

Stationary sources contribute to the ambient particulate burden through three distinct mechanisms. Two are normally considered together as the formation of "primary" particulate emissions from sources, and the third is the formation of "secondary" aerosols, such as sulfates formed from SO_2 and organic smogs formed from photochemical processes. Primary emissions are composed of (1) materials that are in particulate form (solid or liquid) in the gas stream before and after discharge to the atmosphere and (2) materials that are in the vapor phase before discharge but that rapidly condense to the particulate form when they are discharged into and cooled by mixing with ambient air.

Because condensation takes place preferentially on small particles, condensable matter is concentrated primarily in the PM_{10} fraction (particulate matter less than $10\ \mu\text{m}$ in diameter) of source emissions. Since the basis of the standard for ambient air particulate concentrations has been changed from total particulate concentration to PM_{10} concentration, quantitative data on emission rates of condensable matter will be needed to set up State Implementation Plans for compliance with ambient air PM_{10} standards. However, current methods for measuring particulate emissions usually exclude the condensables fraction.

The problem of dealing with condensable matter in emissions regulations has long been a difficult one. During the development of EPA Method 5 (the reference method for measuring particulate emissions) arguments were advanced for specifying a sample collection temperature in the normal ambient range so that condensable matter at ambient temperature would be included. Practical considerations, especially of filter wetting due to condensed moisture, led to the exclusion of condensables at ambient temperature through the Method 5 filter temperature specification of $248 \pm 25^\circ\text{F}$, which is above the boiling point of water.¹ Proposals were also made to include the evaporative residue of the Method 5 impinger catches, commonly called the back half, as part of the total emissions, considering this material to be composed of condensable matter. The ratios of the front-half and back-half particulate catches from Method 5 emission measurements of controlled sources in a number of industries are given in Table 1.² As can be seen from the table, the back half of the Method 5 catch on controlled sources is typically about 20 to 50% of the combined front-half and back-half totals and ranges from a few percent to more than 90%.² Strong objections were raised to the inclusion of the back half as part of the particulate emission measurement, and it was dropped in the promulgated version of Method 5. However, the back-half catch has been included in one form or another for some specific industries and for general application by some states and local control districts.

Efforts are now being made to develop a reference method to quantify the condensables fraction separately from measurements of the particulate portion of primary emissions from stationary sources. In addition, a working definition for condensable matter emitted from stationary sources must be established

Table 1. EPA METHOD 5 TEST RESULTS—RATIO OF FRONT-HALF (FILTERABLE)
TO BACK-HALF PARTICULATE MATTER BY SOURCE TYPE

Source type	Particulates, %		Number of test reports
	Filterable	Back half	
Anode baking furnace	65.8	34.2	7
Asphalt plants	67.9	32.1	17
Boiler/coal (industrial)	90.1	9.9	10
(utility)	55.6	44.4	15
Boiler/oil	42.7	57.3	27
Boiler/wood	84.0	16.0	14
Brick and tile kilns	72.2	27.8	9
Chemical production			
Potassium still	65.3	34.7	1
Chrome oxide kiln	94.3	5.7	1
Boric acid	44.1	55.9	2
Electric arc furnaces			
BOF	62.9	37.1	3
Open hearth	77.3	22.7	3
Coke ovens	71.7	28.3	4
Sandblast	68.2	31.8	2
Heat treating	69.9	30.1	2
Elemental phosphorous	46.0	54.0	1
Fiberboard dryer	57.5	42.5	2
Glass plant	73.0	27.0	14
Grain dryers	74.5	25.5	3
Incinerators			
Municipal	69.7	30.3	4
Industrial	35.3	64.7	1
Sewage sludge	61.8	38.2	2
Iron and steel			
Iron foundries	76.4	23.6	6
Iron and steel sinter plants	70.8	29.2	14
Kraft pulp			
Recovery boilers	85.7	14.3	10
Lime kiln	60.9	39.1	6
Smelt dissolve tank	83.8	16.2	6
Lime kiln	89.6	10.4	3
Mineral products			
Gypsum	87.3	12.7	1
Clay dryer	0.5	99.5	1
Feldspar dryer	11.6	88.4	1
Clay kiln	87.4	12.6	2
Mineral wool	60.7	39.3	3
Petroleum refineries			
Heaters	45.6	54.4	1
FCC	76.1	23.9	2
Catalytic regenerator	46.6	53.4	3
Portland cement			
Kiln (gas-fired)	90.1	9.9	1
(coal-fired)	73.8	26.2	1
(wet-process)	65.5	34.5	8
(dry-process)	37.9	62.1	1
Finish mill (wet-process)	73.6	26.4	3

(continued next page)

TABLE 1. (Continued)

Source type	Particulates, %		Number of test reports
	Filterable	Back half	
Primary nonferrous smelters			
Zinc sweat kiln	24.7	75.3	1
Zinc fume kiln	86.6	13.4	1
Zinc ore briquet dryer	82.7	17.3	1
Lead sinter line	95.6	4.4	2
Lead blast furnace	37.7	62.3	1
Copper converter	69.5	30.5	1
Copper converter, electric arc furnace, and fluid bed roaster	39.8	60.2	1
Copper reverberatory furnace	44.5	55.5	1
Copper roasters	99.0	1.0	1
Molybdenum roasters	97.0	2.9	1
Roofing			
Saturated felt	55.7	44.3	2
Asphalt blowing	56.8	43.2	4
Secondary metal smelters			
Aluminum dross furnace	11.1	88.9	1
Aluminum furnace	33.7	66.3	1
Lead furnace	44.2	55.8	7
Lead mill	47.2	52.8	1
Lead grid casting	52.3	47.7	4
Lead remelt pot	89.8	10.2	1
Nonferrous metal reclamation furnace	64.5	35.5	3
Silicon carbide furnaces (Acheson furnace)	68.3	31.7	4
Spray paint booths	62.2	37.8	4
Textile			
Dryers	24.7	75.3	1
Tenter frame	14.1	85.9	4
Wood products			
Sanding	73.4	26.6	3
Resawing	91.7	8.3	2

^aTest results reflect emissions after air pollution control equipment.

to develop a reference method. A review of possible techniques was conducted from which recommendations are made for the optimum approach for development of routine field sampling procedures for measuring condensable emissions. The following objectives were considered desirable:

- The sampling system should be kept as small as possible.
- The method should incorporate isokinetic traversing if necessary. In-leakages of ambient air upstream of the sampling location can lead to nonuniform concentrations of gaseous (vapor phase) components of the flue gases (e.g., condensables). If the pre-existing particulate matter is incorporated in the sample, isokinetic traversing is required to make the sample representative.
- A specific sampling temperature should be selected, because local ambient conditions would give results that varied according to location, season, local meteorology, and even time of day.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The dilution method appears to be one of two suitable approaches for research and development for measuring total primary emissions including condensable matter from stationary sources. This approach by the same physical mechanism forms condensed particulate matter that occurs in actual plumes. Construction of a system with traversing capability that is suitable for field use appears feasible; consequently, this approach is recommended for development and operator training.

Another method is the impinger/condenser approach. This approach requires the least investment in terms of methods development and capital equipment costs (because existing equipment may be adequate). Research and coincidental testing should be designed to reveal the relative scientific merits of the dilution and impinger/condenser approaches.

SECTION 3

APPROACHES FOR MEASURING CONDENSABLE MATTER

To explore the possible options for measuring condensable matter, a working definition of condensable matter is needed. In particular, the quantity of condensable matter that is present can vary because equilibrium vapor pressures and condensation and evaporation rates vary significantly with changes in temperature and other conditions including concentrations. For example, the equilibrium vapor phase concentration of arsenic trioxide increases by more than a factor of 10 as the temperature is increased from 45 to 80°F and increases nearly a hundredfold more between 80 and 135°F.³ Consequently, the partitioning between the vapor and particulate phases of condensable matter will exhibit seasonal variations. From a regulatory point of view, however, the reference method(s) used for measuring condensable matter should provide results that are not dependent on local temperatures. Thus some standard temperature for sample collection is needed, such as 0, 5, 20, or 25°C. The lower temperatures would result in more conservative (or higher) values for emissions of condensables, but the higher temperatures might be more practical for the application of some measurement methods. Whatever temperature is designated to be standard, the operational definition of condensable emissions should be that material collected by the selected reference method(s). This type of definition is now used for particulate matter collected by Method 5.

Furthermore, the fraction of the emitted material that will be found in the particulate phase after the plume has mixed with ambient air and cooled to the local temperature is not constant. Rather, this fraction will be dependent on the amount of dilution that has taken place with air and the amount of the pollutant that was already present in the atmosphere. Thus, the relative concentrations of a number of organic compounds in ambient air show pronounced seasonal variations related to temperature.^{4,5} By this rationale, only those materials with very low vapor pressures at ambient temperatures or which have high emission rates will be constituents of the ambient particulate burden. However, in addition to condensation, some vapor phase materials become incorporated in particulate emissions shortly after discharge from the stack by sorption processes, even though their vapor pressures in the plume are below saturation.⁶ Vapor phase materials from sorption processes may have significant environmental consequences, even at low concentrations. Thus consideration should be given as to whether or not the method(s) to be developed should include these materials from sorption processes.

Measurement of the condensable portion of source emissions as a separate and independent quantity from preexisting particles in the stack might be done in several ways. The first approach could be some adaptation of Method 5. The simplest method would be to include evaporative residues from Method 5 impinger catches - that is, to revive the inclusion of the Method 5 back half with some modification. Alternatively, a temperature-controlled coil-type condenser could be used in a fashion similar to that in Modified Method 5 sampling for organics. These variations of Method 5 would provide data on condensables

separate and distinct from data on existing particulate matter at flue gas temperatures. Second, dilution cooling with conditioned ambient air might be used to simulate the stack-ambient interface, and the condensed material could be collected together with the preexisting particulate matter to which it is attached. The weight of the condensed portion of the catch might then be determined by difference through successive weighings before and after exposing the filter to a high-temperature environment to drive off volatile materials. Collection of the condensable components of flue gases in an aerosolized (particulate) form separate from preexisting particles, however, may be difficult with presently existing technology. Very high supersaturations are needed to induce homogeneous nucleation and condensation from pure vapors and these conditions cannot necessarily be achieved with hot flue gases. In the absence of preexisting particles to act as condensation centers, attempting to cool the gases by means of heat exchangers might cause most of the condensation to take place on the walls of the heat exchangers or in the condensers discussed previously.⁷ Research would be necessary to determine the minimum particle size and gross numbers sufficient for use in dilution methods and to determine whether such particles could be made available without significant effect on condensable weight. Research on other types of nucleation sites might also be considered.

SECTION 4

ADAPTATIONS OF METHOD 5

In considering the back-half catch as described in Method 5 for further development as a vehicle for collecting condensable matter, certain problem areas must be addressed. A protocol must be devised for carrying out the evaporative process to remove the large volumes of water from the impinger solutions while reducing to acceptable levels any losses of the condensable components that are to be measured. Because impingers used in conjunction with Method 5 result in vigorous contact between sample gases and impinger solutions, the potential for reactions with gases that could cause positive measurement biases must be eliminated or minimized.

The potential for reactions of dissolved gases in the impinger solutions to form artifact particulate material was one argument that was pursued vigorously during the original debates regarding the inclusion or exclusion of the Method 5 back half.⁸ Many of the arguments against including the back half concerned the problem of reactions with SO₂ which form sulfates in impinger solutions; however, a nitrogen purge of the impinger solutions immediately after sampling has been shown to effectively prevent this problem.⁹ Such a purge may reduce the concentrations of the more volatile organic compounds in the solutions, which could introduce a negative bias for some condensables. Also, impingers may enhance uptake of gases when sampling for condensable materials with Method 5. Research could be performed to determine if these effects occur at a significant level and to eliminate or minimize them, if necessary. A coil-type condenser may be preferable in this regard. A filter downstream of the impinger/condenser could be used, if necessary, to ensure that no aerosolized portion of the condensate escapes with the spent sample gas. The use of such a filter is called for in the Oregon State Method 7 for condensable matter¹⁰ and in EPA Method 8.¹¹

INTEGRATION WITH PM₁₀ MEASUREMENT

Integration of the impinger/condenser method for measuring condensable matter with the two current PM₁₀ methods is reasonably straightforward. In the case of the constant sampling rate (CSR) method,¹² the addition of the PM₁₀ cyclone to the Method 5 system would be the only necessary hardware modification. Alternatively, the filter could be moved from the Method 5 oven to immediately follow the cyclone for operation in a Method 17 configuration. For application of the Exhaust Gas Recycle (EGR) method,¹³ few changes would have to be made.

SAMPLE RECOVERY AND ANALYSIS

If the process produces known and identifiable condensable compounds, appropriate techniques for extraction and analysis of the specific constituents in the condensate should be made. In this respect the measurement of the condensable component of PM₁₀ emissions is like the methods used now for

quantifying the emissions of compounds found in the back half of Method 5 samples. For cases in which the condensables are unidentified, the techniques used in the Oregon State Method 7 would be a good starting point for methods development. This method calls for extraction of the condensate with both chloroform and diethyl ether by using a separatory funnel. The organic extracts are evaporated at 20°C or lower to remove the solvents, and the remainder of the aqueous condensate solution is evaporated at 105°C or lower. The evaporative residues are then desiccated for 24 h and weighed.

SECTION 5

DILUTION METHOD

A method has not been devised that would duplicate precisely the mixing process of flue gas with ambient air for all of conditions that actually occur. However, methods designed to reproduce the important features of the mixing process for some typical conditions have been devised. All involve the dilution of a sample gas stream that has been maintained at or near stack conditions with ambient air that has been conditioned to varying extents. In some cases, the dilution air is simply filtered to remove existing particles. In others, its temperature and humidity are controlled, and in some cases, scrubbing of vapor phase components from the dilution air is done. Many of these systems have been reviewed by Pan.¹⁴

PARTICLE LOSSES AND SIZE DISTRIBUTION

Particle losses in nozzles, bends, and long runs of tubing such as sampling probes due to impaction, settling, and diffusion make it impossible to convey an aerosol sample for any distance without depleting the concentrations of particles of all sizes to some extent. These losses are not uniform with respect to particle size. Losses from impaction, turbulent deposition, and settling can be severe for particles with diameters larger than a few micrometers, and diffusion tends to remove particles with diameters smaller than about $0.01\ \mu\text{m}$ very rapidly. For instance, probe losses in a conventional Method 5 setup were reported by Elder et al.¹⁵ to be 90% at $13.4\ \mu\text{m}$ and 77% at $3.8\ \mu\text{m}$, decreasing to 10% at $2\ \mu\text{m}$. Because of difficulties in transporting aerosols without incurring significant losses of particles in the larger size classes, the association of condensables with the fine particle end of the aerosol size spectrum may be fortunate for the application of dilution systems.

To assign the condensables portion of the primary emissions from a process correctly with respect to particle size, the actual condensation process that takes place as the emissions mix with ambient air must be replicated.¹⁶ Homogeneous nucleation is unlikely to be important because flue gases and ambient air have sufficiently high concentrations of small particles to act as primary sites for condensation. For ultrafine ($d < 0.1\ \mu\text{m}$) particles, condensation tends to take place at a constant mass rate per unit area of surface,^{17,18} but the dependence falls off to being proportional to the diameter of the particle for diameters greater than about $1\ \mu\text{m}$. In addition, the aerosol number and surface area distributions for almost all ambient aerosols, especially for emissions from stationary sources, are strongly concentrated in the small aerosol sizes. Thus, initially, the bulk of condensation will take place on what were the smaller particles of the original aerosol. The growth rate of the small particles is so great, in terms of change in surface area per unit mass deposited, that the overall mass transfer from vapor phase to particulate phase can be expected to be dominated by particles that were initially in the fine-particle end of the distribution. Thus, for practical considerations, the condensables can be considered to be

associated wholly with what would have initially been the fine-particle portion of the original size distribution of the particulate emissions.

Because the sample must be extracted and transported through a sampling probe to a location outside the duct for a dilution sampling system, the initial size distribution of the particles in the flue gas cannot be completely duplicated. However, in some existing systems designed to reproduce the important features of mixing the plume with ambient air, losses of particles in the critical size range (a few hundredths of a micrometer to a few micrometers) are relatively low. Thus, the size distribution of the condensed particulate matter is not expected to be altered beyond acceptable limits.

STABILITY OF COLLECTED SAMPLES

Maintaining the integrity of condensable particulate samples during and after sampling can be problematic. Losses resulting from the volatilization of condensed materials collected on filters and on impactor substrates have been noted in ambient air sampling. Similarly, uptake of some semivolatile or volatile materials from the flowing sample stream by previously collected particulate matter has been noted in some studies. The former would result in negative biases in the samples, whereas the latter would result in positive biases. Losses by evaporation of previously collected samples might be relatively large for some compounds, but the uptake of vapor phase material is unlikely to result in significant weight increases. The studies in which such effects were noted showed the uptake to amount to trace quantities only. Reactions involving collected material with incoming gases have also been noted to change the composition of some materials during sampling of ambient air.¹⁹⁻²² Again, gravimetric results would not be greatly influenced (but the apparent chemistry of the sample could be).

Losses of collected particulate material during continued sampling of ambient air have been documented in a number of studies. These results may be useful in predicting source sampling behavior which has not been extensively studied. In one study of retention of arsenic trioxide, losses of about 17% of the collected material were noted for 24-h high-volume samples.²³ König et al.²⁴ found losses as high as 78% for a number of polycyclic aromatic hydrocarbons (PAHs) with losses increasing with longer exposure. The bulk of the losses that they observed were attributed to volatilization, but they also suggested that reactions might have contributed in some cases. The greatest losses in their study were from samplers that were in continuous operation for a period of 14 weeks. During that time the concentrations of the PAHs would have undergone large excursions, as would the filter temperatures, so that the incoming gas stream may well have been far below saturation much of the time. At temperatures between 10 and 30°C, the saturation vapor pressure of benzo[a]pyrene, one of the compounds in their study, varies from 0.15 to 160 ng/m³. Similar effects have been found for aliphatic hydrocarbons, carboxylic acids, and PAHs^{4, 23, 24} and for some pesticides, polychlorinated biphenyls, and other semivolatile organic compounds.⁵ Volatilization losses from high-volume ambient air impactor samples were found to be greatest for the fine fraction of

the size distribution.²⁵ This fraction would have been collected by the backup filter, through which the gas stream passes. The exposure of collected material to incoming gas is thus greater for the filter than for the impactor stages, and greater losses might be expected for the filter.

It is possible that these problems related to volatilization and reactions that occur in ambient sampling may be less serious in stack sampling for condensables when the dilution technique is used. In source sampling, concentrations of condensable materials can be expected to be relatively constant, the temperature of the diluted stream is controlled, and the sampling times are much shorter than those used in ambient sampling. Study is desirable to determine if these factors tend to mitigate the problems encountered in the ambient.

MIXING RATES AND RESIDENCE TIME

Dilution systems have been developed over the past 20 to 25 years for use in investigating particulate emissions from stationary sources. Many of these were intended for use in characterizing submicrometer particles as they existed in the stack gases and did not need to account for the effect of condensation; consequently, these systems are not appropriate for measuring an aerosol as it would exist after condensation had taken place. Again, because most of these systems were intended to be operated in a fashion to suppress condensation, the time delay between the mixing (of the sample and dilution flows) and measurement were usually short, typically about a half second. This is much shorter than the time required to reach moderate dilutions in real plumes. A summary of the characteristics of these systems has been given by Felix et al.²⁶

The mixing rates and residence time in the dilution chamber are important for two reasons. First, the degree of supersaturation achieved depends on both the mixing ratio and rate.^{7, 27, 28} The minimum diameter at which an uncharged particle will serve as a condensation site depends on the amount of supersaturation obtained^{28, 29}; thus the degree of saturation affects the fraction of the total number of particles present which can act as condensation sites (or nuclei). The greater the number of active sites, the less the amount of available condensate per particle and thus the less growth each particle will experience. Also with high concentrations of condensation nuclei, the depletion of the condensable vapor is rapid, and equilibrium can be established in a fraction of a second. Thus for sources that have high concentrations of condensation nuclei (approximately $10^{12}/\text{m}^3$), short residence times in the dilution chamber can be tolerated. On the other hand, at lower concentrations of condensation nuclei ($10^{10}/\text{m}^3$) the time required to reach equilibrium can be several seconds.²⁸

Rapid mixing of the cool dilution gas with the hot sample stream promotes attainment of higher supersaturations.²⁷ The latter, in turn, increases the probability of inducing homogeneous nucleation and, at the same time, decreases the minimum particle size that can act as a condensation nucleus. Both of these effects lead to more rapid condensation and a smaller mean particle size

with which the condensable material becomes associated. Mixing (dilution) time constants for turbulent jets are approximately 0.005 s, those for plumes from stationary source stacks are about 0.75 s, and the time to reach final equilibrium in plumes can be expected to be several seconds.³⁰ Because the mixing rates are likely to be relatively low in plumes, dilution systems which employ turbulent jets or similar rapid mixing processes should probably be avoided, and moderately long retentions (several seconds) in the dilution chamber should be obtained if the measurement system is to mimic reasonably well the natural processes in a plume with respect to fine-particle size distribution.

EXISTING SYSTEMS

Several dilution systems for collecting aerosol samples that contain condensable material(s) in the particulate phase have been designed and constructed to simulate the plume dilution process. Most of these systems were developed to investigate health effects of emissions or to obtain qualitative source emissions data (fingerprints) for use in receptor modeling. Some features of these are given in Table 2. A common problem in all of these systems is that the relative humidity of the final diluted gas mixture must be below saturation to avoid problems caused by wetting filters. Also, positive displacement meters cannot be used in the exhaust stream to meter the sample flow because the sample stream has already been diluted at that point. The most common methods for metering the sample flow have been (1) by means of orifice or venturi meters in the incoming sample line or, (2) if only moderate dilution is used, by taking the sample flow to be the difference between the total exhaust flow and the dilution air flow and metering the two flows separately.

Of the systems described in Table 2, only those of Boubel and Ripperton,³¹ Heinsohn et al.,^{32,33} and Williamson et al.^{34,35} collected the entire diluted sample by filtration for gravimetric analysis. The Boubel and Ripperton sampler was based on a high-volume stack sampler and used relatively modest dilution. Consequently, the final sample temperature was high. The high final temperature was maintained to avoid possible problems from moisture condensation in these experiments, which measured benzo[a]pyrene and other polycyclic organic matter. The Heinsohn et al. system was intended for quantifying total primary emissions from stationary sources. Field results obtained with the system show significantly higher emission rates than those measured with conventional methods. Development of the system was discontinued because sample gas flow control became a problem under certain sampling conditions. The system described by Williamson et al. was used to measure the condensable matter in emissions from a number of processes during the development of the Inhalable Particulate³⁶ and the later PM₁₀ emissions³⁷ factor data bases. However, the size of the system and a single point measurement protocol used in applying it made it undesirable for general use. The data obtained with the system did show results that conformed to those given in Reference 2. A scaled-down version of this diluter has been constructed for use in measuring emissions from wood-burning stoves.³⁷

Table 2. DILUTION DEVICES FOR SAMPLING CONDENSABLES

<u>Reference</u>	<u>Sample Rate (scfm)</u>	<u>Res. Time</u>	<u>Dil. Factor</u>
Boubel and Ripperton ³¹ (1963)	20	0.2	2
Heinsohn et al. ³² (1976)	5-1.5	<1	>5
Williamson et al. ³⁴	0.5	6	25
Houck et al. ³⁸ (1982)	2.7 0.5	0.6 1.2	15 40
Stiles ³⁹ (1983)	0.75	0.025	10
Huynh et al. ⁴⁰ (1984)	0.05	0.25	10
Hildemann et al. ⁴¹ (1985)		2 (main)	25
Jantunen et al. ⁴² (1986)	200	120	10
Farber ⁴³ (1987)	9	40	4

The remaining systems³⁸⁻⁴³ for the most part were intended to provide samples for use in obtaining source signatures for source apportionment applications or for use in bioassays. In most cases, the samples were collected from token portions of the diluted stream rather than collecting the entire diluted stream, and quantitative emissions measurements were not intended. Incidentally, results of bioassays from samples taken with dilution systems have shown much greater mutagenicity effects than samples taken at flue gas conditions.³⁴ These findings are a reminder that the composition of condensable matter can be at least as important as the mass emitted.

SECTION 6

RECOMMENDED RESEARCH

To help ensure that the most appropriate and acceptable method was recommended, a number of people in regulatory agencies at the state and federal level, experts in source measurement and characterization, experts in the field of pollutant transport and fate, and experts in the field of ambient sampling and analysis were contacted for advice and ideas. The approach preferred by a majority was that of air dilution cooling rather than condensation in impingers or condensers. However, from the standpoint of ease of sampling it was generally agreed that the Method 5 back-half approach would be preferable. It was noted that research would be necessary to resolve the potential difficulties posed by the large volumes of condensed water and possible reactions of dissolved gases in aqueous solution to form artifacts that could erroneously be counted as condensable matter. In the dilution approach the sample is collected entirely on a filter, where processes such as artifact formation and loss of volatile components would be expected to be similar to those which take place in ambient reference method sampling. Thus source samples taken with a dilution system would be expected to provide a closer match to ambient samples taken downwind in the source plume, possibly making the data more directly applicable to assessing source impact. Because of all the reasons stated in this paragraph, it is recommended that both the impinger catch and the air dilution approaches be selected for development as EPA methods for measuring condensable source emissions. This would not set any precedents in emission sampling methodology because the use of air dilution techniques is already standard in quantifying emissions from mobile sources and from wood-burning stoves.

WORKING DEFINITION OF CONDENSABLES

Because the split of any condensable component of emissions from a source between the vapor and condensed phases depends on temperature (and for some compounds, the amount of dilution that has taken place and background concentrations of the material), it is recommended that total condensable emissions be defined as the material measured by the sampling train selected by EPA for collecting condensable matter. Just as particulate emissions for regulatory purposes have historically been defined as the front-half catch of Method 5, primary emissions that include condensable matter would be defined by the catch of the dilution sampling train, inclusive of the nozzle through the filter. Again, no precedent is set by such a definition because similar definitions have been used for defining particulate emissions from mobile sources, from wood-burning stoves, and for particulate matter for Method 5.

SUGGESTED DILUTION SAMPLING METHOD

A sketch of the suggested sampling system, identifying key parts, is shown in Figure 1. The use of low mixing rates to preserve, insofar as possible, the detailed size-distribution characteristics that would develop in the actual

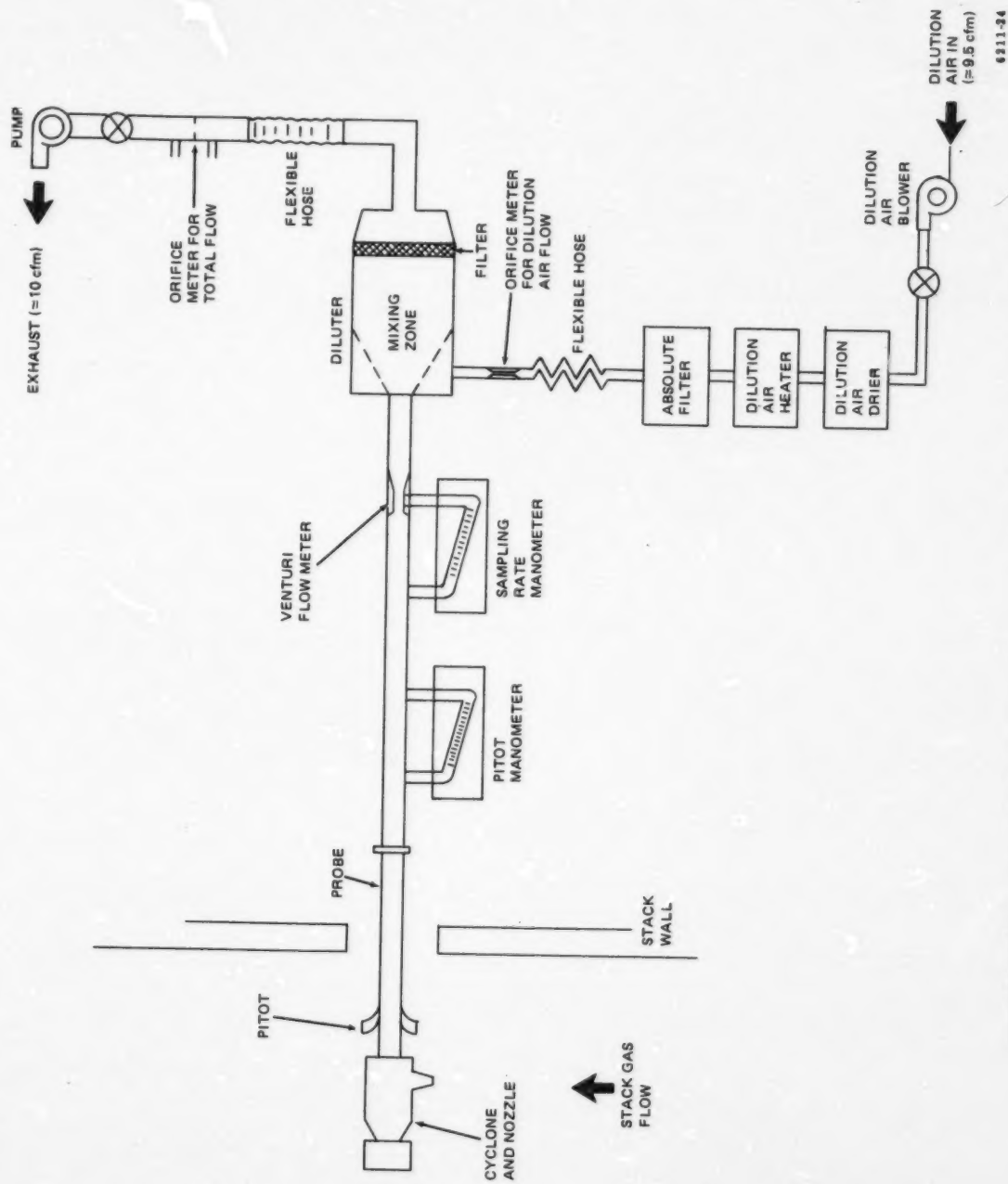


Figure 1. Suggested dilution sampling system for the measurement of primary particulate emissions, including condensables.

plume was not considered to be an important factor by most of the experts who provided advice. Most respondents felt that recovery of an accurate size distribution was unnecessary and possibly not feasible. By foregoing any attempt to preserve the detailed particle size distribution of the final aerosol, rapid mixing of the incoming sample stream and the dilution air can be used. This permits the design of a compact diluter and keeps the weight and size of the device at a minimum.

To minimize the size and power requirements of the system for use in the field, a total flow of about 280 L/min (10 cfm) is suggested, with a sample flow of about 14 L/min (0.5 cfm). This sample flow is comparable to the flow normally used in Method 5 sampling (0.75 cfm). In many instances, a higher sample flow would not allow enough dilution to avoid moisture condensation problems without requiring a higher flow of dilution air, which would in turn require the apparatus to be larger than might be desired. The cyclone shown at the probe inlet is provided to hold deposition of particulate matter to acceptably low levels to ensure that the sample flow meter functions properly. A cyclone that removes particles with aerodynamic diameter larger than nominally 2.5 μm is recommended for this purpose on the basis of experience with similar systems. This also provides a convenient device for measuring total emissions of fine particles if they are defined as those nominally 2.5 μm and smaller.

The diluter illustrated is based on a design used by Southern Research Institute (SRI) for quantitative dilution of aerosol samples for making size distribution measurements of ultrafine aerosol particles. Working versions of the SRI diluter for a total flow of 7 cfm have provided complete mixing of the sample and dilution flows within a distance of 12 in. downstream of the sample inlet. A similar diluter, 6 in. in diameter and 1.5 ft long, that was scaled for a total flow rate of 10 cfm would provide a 1.5 s retention time for condensation which is a generous amount given the rates at which condensation takes place. A 6-in diameter filter at the exit end of the diluter would operate at a face velocity of about 60% of the face velocity of a conventional ambient air high-volume filter unit and thus should provide adequate loading capability.

Conditioning recommended for the dilution air includes filtration to remove background particulate matter and drying to a dew point of 35°F (1.5°C), with a final temperature of 68°F (20°C). The low dew point and moderately high dilution ratio should prevent problems of moisture condensation for most flue gases that might be encountered.

Because the sample flow is only a small part of the total flow, measurement of the sample flow at the exhaust end of the system, as in Method 5, is not possible in the recommended setup. Instead, a flow-metering element is recommended immediately upstream of the sample inlet to the diluter. A venturi-type flow meter is recommended, but other types might be used. A Method 5 dry gas meter cannot be used to obtain the integrated sample volume, but an electronic flow totalizer that uses the signal from the sample flow meter could be used for that purpose. This approach for obtaining the integrated gas volume is similar in principle to that used in Method 5 in which

the sampling rate is set and maintained at isokinetic rates by using an orifice meter, and the total gas volume sampled is found at the end of the run from an integrating dry gas meter. A requirement of Method 5 is that the average sampling rate be within $\pm 10\%$ of isokinetic as determined from the dry gas meter. Typically, the deviation from isokinetic is closer to $\pm 5\%$. Although the final check is made from the dry gas meter volume, it is the orifice meter that has actually provided the required sampling rate. Thus, although the use of integrated sample volumes from the venturi meter suggested for the condensables sampling train may not provide the accuracy of the Method 5 dry gas meter, it should be sufficiently accurate for the purpose when the venturi meter is properly calibrated and used.

SAMPLING PROTOCOL

The suggested sampling protocol for a measurement of total emissions including condensable matter parallels that of Method 5 in most respects. A nozzle of appropriate size for the design sampling rate of the system and the gas velocities in the stack would be mounted on the cyclone inlet. A standard Method 5-type traverse pattern would be used in sampling, and the sampling rate would be set according to the venturi meter readings and adjusted as needed to maintain isokinetic sampling conditions. During sampling, an electronic integrator would be used to obtain the total gas volume sampled. Measurement of stack moisture content might be made by condensers and driers on the sampler exhaust stream or by a parallel Method 4 sample. Calibration checks of the sample flow meter via a dry gas meter or a calibration orifice are suggested as required procedures prior to and immediately following each run. This protocol does not maintain a fixed dilution ratio, but the variability induced will not pose a problem. A minimum acceptable dilution factor should be specified (which would in turn set a maximum sampling rate); the nozzle size to be used for a traverse would then be selected to ensure that the minimum dilution specification is not violated.

The dilution train will not provide a direct measure of the split between condensable matter and preexisting particulate material in the flue gas unless use of a filter in the train can be developed. However, by running a parallel Method 17 sample, the split could be found by difference. For example, dual measurements were made by using a modification to Method 17 in conjunction with the "Source Dilution Sampling System" while emissions factor data were being collected as part of the EPA Inhalable Particulate Program.

By mounting a PM_{10} cyclone upstream of the cyclone at the probe inlet, a measure of PM_{10} emissions that includes the condensable fraction can be obtained. The CSR protocol¹² could then be applied to carry out the traverse at a fixed sampling rate as required to maintain size fractionation at $10\ \mu m$.

VERIFICATION OF THE PERFORMANCE OF THE METHOD

A number of performance verification checks and proofs should be carried out during the development of the method. These include but may not be restricted to the following:

1. Test for the deposition of particles and condensable vapors on the internal surfaces of the system.
2. Determination of the accuracy of flow metering and flow totaling by the venturi meter.
3. Laboratory verification of the effectiveness of the collection of condensable materials by analyzing for a number of classes of compounds that might be expected to be of importance in the field.
4. Determination of relative accuracy of emission rate results with Methods 5 or 17 in sampling process streams that are free of any significant concentration of condensables.
5. Determination of the precision of the method in sampling both condensing and noncondensing streams.
6. Measurement of elution of previously collected condensed materials from the filter during sampling with compounds of different classes.
7. Characterization of the effect of permitting a variable dilution ratio.

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